A PILOT-SCALE STUDY OF THE FORMATION OF ASH DURING PULVERIZED LOW-RANK COAL COMBUSTION

John Hurley
University of North Dakota
Energy and Environmental Research Center
Grand Forks, North Dakota 58202

Keywords: char morphology, transmission electron microscopy, submicron ash

INTRODUCTION

In 1987 over 250 million tons of coal mined in the western-coal producing region of the United States was purchased by electric utilities (1,2). The goal of the utilities is to convert the chemical energy in the coal to electrical energy that can be sold at a profit. The most common conversion method involves pulverizing the coal and burning it in a boiler system. The steam produced is passed through a turbine which is used to turn an electrical generator. Unfortunately, because of the high temperatures present in a utility boiler, the ash formed during the combustion of the coal can cause a number of operational problems and can reduce the efficiency of the energy conversion process.

In an effort to delineate a portion of the process of ash formation during combustion of pulverized western U.S. low-rank coal, subbituminous coals from the Eagle Butte mine, WY, and the Sarpy Creek mine, MT, were burned in the Penn State down-fired combustor. Entrained particulate matter was collected at several stages of combustion. The particulates were analyzed by thermogravimetry, x-ray diffraction, computer-controlled scanning electron microscopy, and transmission electron microscopy (TEM) in order to discern changes in size and association of the inorganic matter during the combustion of the coal. Due to space limitations, the data and discussion presented here focus only on the TEM observations of the Eagle Butte coal as well as samples of the char and submicron ash particles produced during combustion.

EXPERIMENTAL

To properly understand the ash formation process, a knowledge of the time-temperature history and interactions of ash particles is required. Therefore, the Penn State down-fired combustor was designed for self-sustained combustion of pulverized coal in a nonrecirculating and nonswirling flame and to provide easy access for sampling at all stages of combustion. The combustor is described in depth elsewhere (3). It is illustrated in Figure 1.

Before firing with pulverized coal, the combustor was preheated on natural gas until the wall temperature profile approximated that encountered when firing the coal to be tested. During testing the coal feed rate was held at 200,000 Btu/hr which yielded a volumetric heat release rate of about 20,000 Btu/hr/ft^3. Particulate sampling commenced as soon as a stable temperature distribution occurred above the sampling point. Particulate samples were collected at three ports, the top (port 1), second from the top (port 2), and from immediately above the accelerator at the bottom of the furnace (port 10). A four-stage multicyclone system, housed in a convective oven during sampling, was used to separate the particulates from the gas.

The morphologies of char and submicron inorganic particles were characterized by transmission electron microscopy (TEM). In order to allow analysis of particles that were included within a coal or char matrix, the samples were prepared by embedding them in LR White resin, then cutting ultrathin sections with the use of a Reichert Jung Ultracut E ultramicrotome. Only silver, gold, and violet sections were selected for analysis. The colors were an interference effect and indicated that the sections were between 0.08 to 0.2 μm thick (4). The TEM-STEM system used was a Phillips EM420 with a Link Systems 860 Series II x-ray analyzer.

RESULTS AND DISCUSSION

Coal Samples: TEM observations of ultrathin sections of the Eagle Butte coal showed that, in addition to larger irregularly shaped minerals, approximately one in four coal particles contained concentrations of small, high contrast inclusions with circular cross sections. A TEM photo of the edge of such a coal particle is shown in Figure 2. The inclusions occurred mainly in three distinct size ranges. The smallest particles had diameters of approximately 2 to 3 nanometers. They were evenly dispersed, although they were more easily visible in the thinner (lighter) portions of the coal section. A second size class of the inclusions had diameters between 20 and 30 nanometers. They did not appear to be as evenly dispersed across the coal particles as was the smallest size range. The largest size class was composed of particles with diameters greater than approximately 60 nanometers, although this size range was not completely distinct from the middle size range (i.e., there was some gradation between them).

The composition of the smallest high contrast inclusions was difficult to discern. Although the small inclusions strongly scattered the electron beam, electron diffraction was not practical because beam heating of the epoxy matrix caused the position of the particles to continually shift relative to the beam. Energy dispersive x-ray analysis of the smallest inclusions was also inconclusive because of the low signal to noise ratio in the EDS signal, although after counting times of several minutes, a signal did emerge in the EDS spectra of individual small particles or groupings. For the Eagle Butte coal the signal usually showed the presence of calcium, iron, and sulfur. Also, the source of the signals was obscured by the fact that calcium and sulfur, and possibly iron, are associated directly with the organic portion of the coal. Since the ultrathin section was approximately 100 nanometers thick, and the smallest particles were 2 nanometers in diameter, it was impossible to tell if the x-ray signal was emitted from organically associated elements or the particles. Although sodium and magnesium are also associated with the organic matrix, the detector may not have indicated the presence of those elements because they are present in lower concentrations, and the detector is not very sensitive to the K_α lines of those elements. In general, it was found that clear x-ray signals could only be obtained from particles that had diameters above several tens of nanometers, although some smaller particles gave strong x-ray signals if they were composed of high atomic number elements.

Because a strong x-ray signal from the small, high contrast inclusions was not clear, the possibility existed that the small inclusions were not inorganic. Friel and others have shown the formation of mesophase spheres upon heating of several bituminous coals (5). The spheres they reported had the size and appearance of the medium size high contrast inclusions shown in Figure 2. However, several lines of evidence supported the conclusion that the small inclusions shown in Figure 2 were not similar to mesophase spheres. First, the coal had not been heated prior to analysis. Since mesophase usually forms on heating, one would not expect mesophase spheres to be present in the coal. However, some heating of the sample may have occurred in the TEM through absorption of energy from the electron beam. Second, the Eagle Butte and Robinson coals are subbituminous coals. Subbituminous coals do not usually form mesophase spheres upon heating. Third, and most convincing, a close examination of the boundary between the coal particles and the resin shows that some of the smallest particles have separated a small distance from the coal and reside in the resin. Mesophase spheres would not be expected to separate from the matrix.

Port 1 Samples: By the time the particulates reached the top port (port 1), the coal had undergone 50.8% burnout. The residence time of the particles in the radiant zone above that port was approximately 0.07 seconds. The maximum equilibrium temperature experienced by a nonreacting inorganic particle before sampling was approximately 1220°C.

Two main types of char particles were seen in the port 1 particulate samples: those that were highly vesicular and those that showed little internal structure. In general, the appearance of the char was essentially identical to the appearance of the char collected at port 2, so further discussion of char morphologies will be saved for the discussion of the port 2 chars.

Port 2 Samples: By the time the particulates reached port 2, the coal had undergone 96.3% burnout. The total residence time in the refractory lined portion of the combustor was approximately 0.2 seconds. The maximum equilibrium temperature reached by a nonreacting particle by the time it reached the sampling probe was approximately 1310°C. That temperature was reached immediately before the probe.

As in the case of the port 1 samples, two main types of char were evident in the ultrathin sections of the port 2 samples: highly vesicular particles and higher density particles that contained much less void space. Figure 3 is a 10,500x TEM photograph of a vesicular char particle. The thin walls of such particles suggest that they may fragment easily during combustion. The ash particles associated with such chars tend to be large globules lightly attached to either internal or external char surfaces. In addition to the large ash globules, the char particles contained high levels of the 3 and 30 nanometer particles seen in the coal. These particles are shown in Figure 4, which is a 82,000x TEM photograph of the char particle in Figure 3. The smallest inclusions underwent little change during the early stages of combustion.

The appearance of a high concentration of the small, high contrast inclusions shown in Figure 4 was an artifact of the difference in electron transmissivity of the char and the inclusions. In actuality, the thickness of the char surrounding the inclusions (the char is not obvious in the figure) was approximately 500 times the thickness of the smallest particles. Assuming that the particles had a density equal to that of quartz (2.6 g/cm^3), whereas the bulk char (i.e., carbonaceous and noncarbonaceous) had a density equal to the density of coal (1.3 g/cm^3), and that the average concentration of the particles in the char was equal to the concentration of particles shown in Figure 4 (a liberal assumption), the weight percent of the smallest inclusions can be, at most, 0.15% of the weight of the char. Assuming the concentration was the same in the coal and that the inclusions formed ash in a weight ratio of 1:1, then only about

2.5% of the weight of the ASTM ash was formed by the smallest inclusions. The mass concentration of the next larger class (30 nanometers) was approximately 0.5% of the char or 8.6% of the ash.

Figure 5 shows a TEM photograph (4,900x) of the second type of char particle, the type that showed much less void space than the highly vesicular char. Like the vesicular char, the two smallest size classes of high contrast inclusions were sometimes found in the more dense char particles. The inclusions in the higher density char collected at port 2, however, showed some coalescence which caused the distinctions between the size classes to become less pronounced. Unlike the smallest high contrast inclusions, the large globular particles of ash often associated with the highly vesicular chars were absent. This may have been because this type of char particle burned more slowly, so that particle coalescence was relatively slow and because the ash particles were shed from this type of char at a relatively high rate. Figure 5 is also interesting in that it shows two physical features of the ultrathin sections. First, grooves in the section, generally running right to left and sloping upwards slightly to the left, are caused by imperfections in the knife edge, most commonly remnants of previously cut sections. In addition, wrinkles in the ultrathin section can clearly be seen. The wrinkles generally run vertically or point toward the char section. The closeness of the wrinkles gives a visual indication of the ratio of length or width to thickness of the ultrathin sections. The typical dimensions of ultrathin sections are 0.7 mm long and 0.1 μm thick, so the length to thickness ratio is approximately 7000 to 1. The length to thickness ratio of writing paper is approximately 4000 to 1.

<u>Port 10 Samples</u>: By the time the particulates reached the sampling probe at port 10, the coal had undergone 99.8% burnout. The total residence time in the refractory lined portion of the combustor was approximately 2.4 seconds. The equilibrium temperature of a nonreacting particle at port 10 was approximately 1055°C.

Although uncommon, some char particles were still evident in the port 10 samples. Only the more dense char particles were seen however, indicating that the more vesicular char particles had burned out. Figure 6 is a TEM photograph (10,500x) of a portion of a char particle showing how the small, high contrast inclusions have melted. In some instances the particles coalesced to form particles with diameters in the 0.1 μm range. In other cases, the melted particles appeared to have flowed through pores within the char. The longer chain of flow regions running left to right across the photograph contained mostly iron. The large particle at the right edge of Figure 6 contained high concentrations of aluminum and silicon, with smaller amounts of nickel, chromium, and iron (possibly stainless steel). As was the case with the more dense char particles collected at port 2, no large globules of ash were seen at the surface of this type of char.

CONCLUSIONS

TEM observations of the coals indicated two main types of char form. One type was highly vesicular and burned out before the other more dense char. The thin walls of the highly vesicular char particles suggested that they may fragment easily, leading to the formation of several ash particles per char particle. However, the relatively few ash globules associated with the surfaces of the denser char particles indicated that less coalescence and more rapid shedding of ash particles occurred from the denser char than from the more vesicular char. Since the two chars most probably formed from different maceral types, a coal containing higher concentrations of the maceral that forms the higher density char may produce more and smaller ash particles per coal grain than a coal having lower concentrations of the maceral type.

Approximately one in four coal particles contained concentrations of small, high contrast inclusions with circular cross sections. The inclusions fell into three size categories: 2 to 3 nanometers, 20 to 30 nanometers, and greater than 60 nanometers. EDS data indicated that the inclusions were composed primarily of calcium, sulfur, and iron, although the data was not conclusive. The inclusions were believed to be inorganic particles rather than organic regions such as mesophase. Calculations showed that, at most, 11% of the ash could be formed from the particles in the smallest two categories. The assumptions in the calculations were very liberal, so the actual weight was believed to be no more than 1%, within the range of the weight of fume produced during coal combustion. However, a great deal of coalescence of the inclusions occurred in later stages of particle combustion, so the importance of the inclusions in fume formation was not clear.

REFERENCES

1. U.S. Department of Energy, "Coal Production 1987", DOE/EIA0118, p 29 (1988).

2. U.S. Department of Energy, "Coal Distribution January/December 1987", DOE/EIA0125 (1988).

3. Hurley, J.P., "A Pilot-Scale Study of the Formation of Ash During Pulverized Low-Rank Coal Combustion", Ph.D. Thesis, The Pennsylvania State University (1990).

4. Peachey, L.D. "Thin Sections I. A Study of Section Thickness and Physical Distortion Produced During Microtomy", Journal of Biophysical and Biochemical Cytology, 4, 3, 233-245, 1958.

5. Friel, J.J., Mehta, S., Mitchell, G.D., Karpinski, J.M. "Direct Observation of the Mesophase in Coal", Fuel, 59, 610-616, 1980.

6. U.S. Department of Energy, "Combustion Inorganic Transformations", report for the period April 1988, to June 1989, DEFC2186MC10637 (1989).

ACKNOWLEDGEMENTS

Most of the funding for the research was provided by the U.S. Department of Energy under the Combustion Inorganic Transformations project, contract DEFC2186MC10637, Phillip Goldberg, COTR; and the Commonwealth of Pennsylvania under the Coal/Water Slurry Program. In addition, the author would like to thank Harold Schobert of Penn State and Steven Benson of the University of North Dakota Energy and Environmental Research Center for their support.

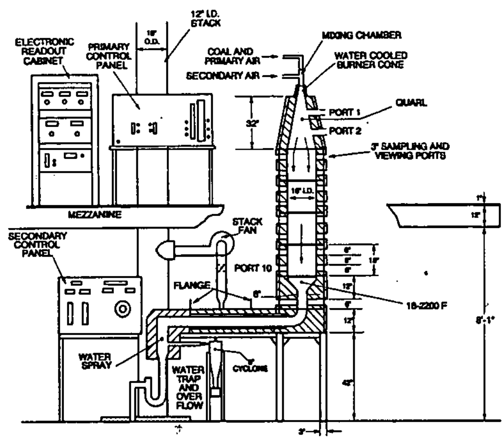

Figure 1. The Penn State down-fired combustor.

Figure 2. TEM photograph of an Eagle Butte coal particle containing high levels of high contrast inclusions.

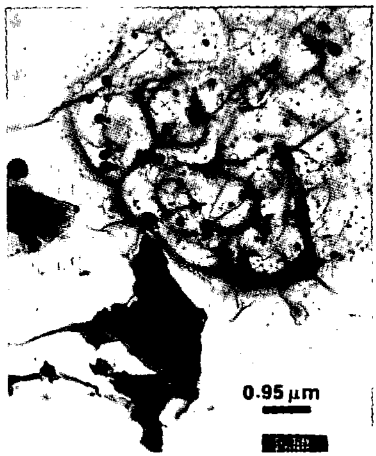

Figure 3. TEM photograph of vesicular Eagle Butte char particles showing large numbers of ash globules associated with both interior and exterior char surfaces.

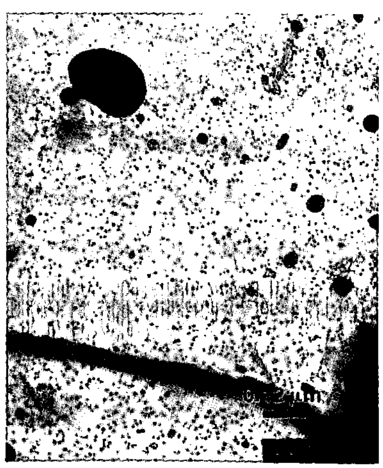

Figure 4. TEM photograph of the char particle shown in Figure 3 illustrating the unchanged nature of the 3- and 30-nanometer diameter contrast inclusions.

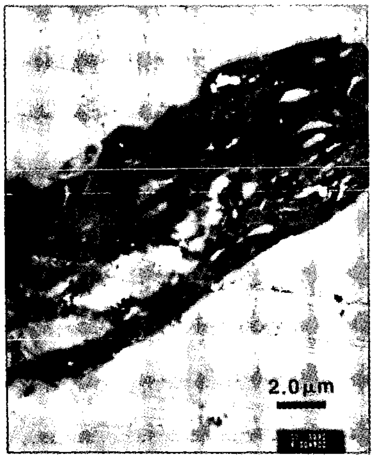

Figure 5. TEM photograph of a high density Eagle Butte char particle collected at port 2.

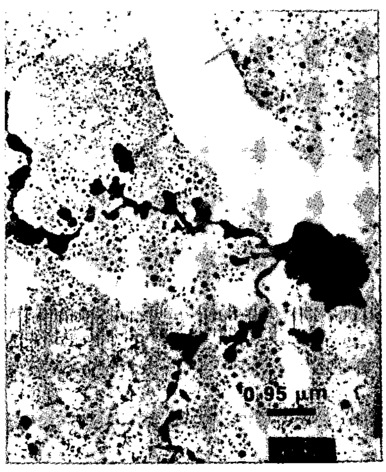

Figure 6. TEM photograph of a frozen flow of molten ash within pores in an Eagle Butte char particle collected at port 10.